10.603.274
09.22.03

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Patentanmeldung Nr. Patent application No. Demande de brevet n°

02078742.0

Der Präsident des Europäischen Patentamts;
Im Auftrag

For the President of the European Patent Office

Le Président de l'Office européen des brevets
p.o.

R C van Dijk

Anmeldung Nr:
Application no.: 02078742.0
Demande no:

Anmeldetag:
Date of filing: 04.09.02
Date de dépôt:

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Bezeichnung der Erfindung/Title of the invention/Titre de l'invention:
(Falls die Bezeichnung der Erfindung nicht angegeben ist, siehe Beschreibung.
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Si aucun titre n'est indiqué se referer à la description.)

FCC Catalyst for reducing the sulfur content in gasoline and diesel

In Anspruch genommene Prioriät(en) / Priority(ies) claimed /Priorité(s) revendiquée(s)
Staat/Tag/Aktenzeichen/State/Date/File no./Pays/Date/Numéro de dépôt:

Internationale Patentklassifikation/International Patent Classification/
Classification internationale des brevets:

C10G/

Am Anmeldetag benannte Vertragstaaten/Contracting states designated at date of filing/Etats contractants désignées lors du dépôt:

AT BE BG CH CY CZ DE DK EE ES FI FR GB GR IE IT LI LU MC NL PT SE SK TR

FCC CATALYST FOR REDUCING THE SULFUR CONTENT IN GASOLINE AND DIESEL

The present invention relates to a catalyst composition comprising zeolite, alumina, anionic clay and kaolin, its preparation and its use in FCC.

Environmental concerns have resulted in legislation limiting the sulfur content in fuels, such as gasoline and diesel. Sulfur, when present in gasoline, not only contributes to SOx-emissions, but also poisons car engine exhaust catalysts. One way of reducing these sulfur levels is hydrotreating. However, such a process requires substantial capital investments and operation costs. It would be more desirable to reduce the sulfur content *in situ*, i.e. during processing in the FCC-unit.

WO 99/49001 and T. Myrstad et al., *Appl. catal. A* 187 (1999) 207-212 disclose such an *in situ* process using a composition comprising a hydrotalcite material impregnated with a metal additive, i.e. a Lewis acid, preferably Zn. According to this document, the impregnated hydrotalcite material can be incorporated in the matrix of an FCC catalyst. Impregnation generally leads to (a) an inhomogeneous distribution of the metal additive in the hydrotalcite material whereby the metal is mainly deposited on the outer surface of the hydrotalcite particles, (b) precipitation of the metal additive as a separate phase next to the hydrotalcite material.

The so-obtained metal distribution facilitates leaching of the metal additive into the aqueous suspension during the preparation of the catalyst composition. This leads to a decrease in metal-content of the anionic clays (with consequently a loss in catalytic activity), together with precipitation of the metal additive on th alumina present in the suspension. The presence of such metal-containing alumina in the catalyst composition can lead to several side reactions (e.g. coke formation) during use in FCC.

During use of the catalyst, which consequently leads to abrasion of the catalyst and the anionic clay, microfines (dust) will be formed. If the metal additive is located mainly on the outer surface of the anionic clay particles and/or if the additive is present as a separate phase within the catalyst, the microfines will contain relatively large amounts of the metal additive. This is environmentally undesired, especially when the additive is a heavy-metal-containing compound. Furthermore, with the removal of the metal additive from the catalyst, catalytic activity will be lost.

The present invention provides a catalyst composition comprising 5-55 wt% metal doped anionic clay, 10-50 wt% zeolite, 5-40 wt% alumina, 0-10 wt% silica, 0-10 wt% of other ingredients, and balance kaolin.
In metal doped anionic clays, the metal additive, i.e. the metal dopant, is better distributed within the anionic clay, without separate phases of metal being present. Hence, microfines resulting from abrasion of this catalyst composition will contain less of the metal additive than microfines resulting from the prior art catalyst composition. Furthermore, less metal will leach out from these doped anionic clays during catalyst preparation then from impregnated anionic clays.

Moreover, it has been found that the use of catalyst compositions according to the invention results in a higher reduction of sulphur in fuels such as gasoline and diesel than the use of compositions comprising impregnated anionic clay.

<u>Metal doped anionic clay</u>

Anionic clays have a crystal structure which consists of positively charged layers built up of specific combinations of divalent and trivalent metal hydroxides between which there are anions and water molecules. Hydrotalcite is an example of a naturally occurring anionic clay wherein Mg is the divalent metal, Al is the trivalent metal, and carbonate is the predominant anion present.

Meixnerit is an anionic clay wherein Mg is the divalent metal, Al is the trivalent metal, and hydroxyl is the predominant anion present.

A variety of terms is used to describe the material that is referred to in this specification as an anionic clay, such as hydrotalcite-like material and layered double hydroxide. In this specification we refer to these materials as anionic clays, comprising within that term hydrotalcite-like materials and layered double hydroxides.

The difference between impregnated and doped anionic clays is that doped anionic clays are prepared by a process wherein the metal additive(s) (hereinafter referred to as metal dopant(s)) is/are present during the formation of the anionic clay, whereas impregnation is always performed after th formation of anionic clay has been completed.

The metal dopant can be part of the anionic clay structure, by replacing a part of the divalent or trivalent metal, or can be positioned between the divalent and trivalent metal layers of the anionic clay.

There are several methods to prepare anionic clays. The first preparation method involves co-precipitation of a divalent and a trivalent metal source out of an aqueous solution, followed by aging the precipitate. Optionally, the aged precipitate is themally treated and rehydrated. Before or after thermal treatment and/or rehydration, the anionic clay can be shaped to form shaped bodies.

The second preparation method involves mixing a trivalent metal source and a divalent metal source in aqueous suspension and aging the mixture to form an anionic clay, optionally followed by a thermal treatment and a rehydration step. Before or after thermal treatment and/or rehydration, the anionic clay can be shaped to form shaped bodies.

The third preparation method involves mixing a divalent and a trivalent metal source in aqueous suspension, shaping the mixture to form a shaped body, optionally calcining the shaped body, and aging the shaped body in aqueous suspension to form an anionic clay-containing body, optionally followed by a

thermal treatment and a rehydration step. Before shaping, some anionic clay, preferably 5-75 wt% of the final amount, might have been formed, although at least a part of the final amount of anionic clay is formed after shaping.

The metal dopant(s) can be introduced in any of the applied process steps.
In the first preparation method, the metal dopant(s) can be co-precipitated with the divalent and trivalent metal source, it can be added during aging or before or during the optional rehydration, or it can be introduced via a doped seed. Furthermore; metal dopant(s) may be introduced in more than one of these steps.
In the second and third preparation method, the metal dopant(s) can be added to the suspension containing the divalent and trivalent metal source, before and/or during aging. They either are added to the suspension as separat compounds (either as a solid or dissolved in a liquid), or are already present in the divalent metal source, the trivalent metal source, and/or a seed. In the latter case, a so-called metal doped divalent, metal doped trivalent metal, and/or metal doped seed is used.
It is also possible to introduce the metal dopant(s) at a later stage during the preparation, for instance before or during the optional rehydration step.

The term aging refers to treatment of the suspension at thermal or hydrothermal conditions for 30 minutes to 3 days. In this context, hydrothermal conditions mean in the presence of water (or steam) at temperatures above 100°C and pressures above atmospheric, e.g. autogeneous pressure. Thermal conditions refer to temperatures between 15 and 100°C and atmospheric pressure.
The preparation of metal doped anionic clay may be conducted batch-wise or in a continuous mode, optionally in a continuous multi-step operation. The process may also be conducted partly batch-wise and partly continuous.
During this process, acids or bases can be added, for example to control the pH.

If an excess of divalent and/or trivalent metal source is present during aging, compositions of anionic clay and unreacted (meaning: not reacted to anionic clay) divalent and/or trivalent metal source can be formed. Such compositions may for instance comprise Mg-Al anionic clay and boehmite and/or brucite. These compositions can suitably be used in the catalyst composition according to the invention.

After the aging step, the anionic clay is optionally thermally treated to form a solid solution and/or spinel, followed by rehydration of the solid solution to form an anionic clay again. This thermal treatment and rehydration increase th physical strength of the particles.
The thermal treatment can be conducted in an oxygen-containing atmosphere, in a hydrogen-containing atmosphere, in an inert atmosphere or in steam at temperatures varying from 150° to 900°C for a time ranging from a few minutes to 24 hours.
Rehydration is performed by contacting the thermally treated material with a polar liquid, preferably water, at thermal or hydrothermal conditions, preferably at 60-95°C. As mentioned before, metal dopant(s) can be present in the polar liquid during this rehydration step.

As explained above, a shaping step can be performed to obtain shaped bodies. Suitable shaping methods include spray-drying, pelletising, extrusion (optionally combined with kneading), granulation, beading, or any other conventional shaping method used in the catalyst and absorbent fields or combinations thereof. The amount of liquid present in the precursor mixture used for shaping should be adapted to the specific shaping step to be conducted. It might be advisable to (partially) remove the liquid used in the precursor mixture and/or add additional or other liquid, and/or change the pH of the precursor mixture to make the precursor mixture gellable and thus suitable for shaping. Various additives commonly used in the various shaping methods such as extrusion

additives, binders and fillers may be added to the precursor mixture used for shaping.

During the preparation of anionic clay, irrespective of the preparation method used, the solids involved (e.g. solid trivalent metal source, solid divalent metal source, formed anionic clay, formed shaped bodies) can be milled. In this specification the tem 'milling' is defined as any method that results in reduction of the particle size. Such a particle size reduction can at the same time result in the formation of reactive surfaces and/or heating of the particles. Instruments that can be used for milling include ball mills, high-shear mixers, colloid mixers, and electrical transducers that can introduce ultrasound waves into a slurry. Low-shear mixing, i.e. stirring that is performed essentially to keep the ingredients in suspension, is not regarded as 'milling'.
If this milling is performed in suspension, metal dopant(s) can be added during milling.

Suitable trivalent metals for the preparation of metal doped anionic clays includ aluminium, gallium, indium, iron, chromium, vanadium, cobalt, manganese, cerium, niobium, lanthanum, and combinations thereof.
Suitable gallium, indium, iron, chromium, vanadium, cobalt, cerium, niobium, lanthanum, and manganese sources are their respective oxides, hydroxides, carbonates, bicarbonates, hydroxycarbonates, acetates, hydroxyacetates, nitrates, chlorides, chlorohydrates, alkoxides, and clays containing the desired metal.
Suitable aluminium sources include aluminium oxides and hydroxides such as transition alumina, aluminium trihydrate (Bauxite Ore Concentrate, gibbsite, bayerite) and its thermally treated forms (including flash-calcined aluminium trihydrate), sols, amorphous alumina, and (pseudo)boehmite, aluminium-containing clays such as kaolin, sepiolite, and bentonite, modified clays such as metakaolin, and/or alumina salts such as aluminium nitrate, aluminium chloride, aluminium chlorohydrate, and sodium aluminate.

Preferred trivalent metal sources are oxides, hydroxides, carbonates, and hydroxycarbonates, as these materials are relatively inexpensive. Moreover, these materials do not leave anions in the metal doped anionic clay which either have to be washed out or will be emitted as environmentally harmful gasses upon heating.

Suitable divalent metal sources include magnesium, zinc, nickel, copper, iron, cobalt, manganese, calcium, barium, and combinations thereof. Suitable zinc, nickel, copper, iron, cobalt, manganese, calcium, and barium sources are the respective oxides, hydroxides, carbonates, hydroxycarbonates, bicarbonates, acetates, hydroxyacetates, nitrates, chlorides, and clays containing the desired metal.

Suitable magnesium sources include magnesium oxides or hydroxides such as MgO, $Mg(OH)_2$, hydromagnesite, magnesium salts such as magnesium acetate, magnesium formate, magnesium (hydroxy) acetate, magnesium carbonate, magnesium hydroxy carbonate, magnesium bicarbonate, magnesium nitrate, and magnesium chloride, and magnesium-containing clays such as dolomite, saponite, and sepiolite.

Preferred divalent metal sources for the preparation of metal doped anionic clays are oxides, hydroxides, carbonates, hydroxycarbonates, bicarbonates, and (hydroxy)acetates as these materials are relatively inexpensive. Moreover, these materials do not leave anions in the metal doped anionic clay which either have to be washed out or will be emitted as environmentally harmful gasses upon heating.

It should be noted that in case of the first preparation method, which involves co-precipitation of a divalent and a trivalent metal source out of an aqueous solution, both these metal sources have to be water-soluble.

In case of the second and third preparation method, which involves the aging of a divalent and a trivalent metal source in aqueous suspension, it will be clear that either the divalent metal source, the trivalent metal source, or both the

trivalent and the divalent metal source is/are insoluble in water. As the preferred divalent and trivalent metal sources are the oxides, hydroxides, carbonates, and hydroxycarbonates, which are all insoluble in water, it is clear that the second and third preparation method are preferred over the first preparation method.

Either Mg-Al anionic clays, Al-containing non-Mg anionic clays, Mg-containing non-Al anionic clays, or non-Mg non-Al anionic clays can be used.
Preferred anionic clays for the present invention are Mg-Al anionic clays, i.e. those which contain aluminium as the trivalent and magnesium as the divalent metal, having a ratio of divalent to trivalent metal from 0.1 to 10, preferably from 1 to 6 and more preferably from 2 to 4. The most preferred ratio is close to 3.

Suitable Mg-Al anionic clays preferably have either $3R_1$ or $3R_2$ stacking. These two types of anionic clays have a three-layer repeat. They are distinguished from each other by the intensities of the (107) and (018) X-ray reflections. The (107) and (018) reflections are generally positioned close to 45 and 47 degrees 2-theta, respectively. In $3R_2$ type anionic clays the (107) reflection is stronger than the (018) reflection, whereas in $3R_1$ type anionic clays the (018) reflection is stronger than the (107) reflection. The presence of peaks at 45 and 47 degrees 2-theta with comparable intensity suggests the presence of a mixture of these two types of anionic clay. It is to be understood that the precise 2-theta values for the (107) and (018) reflections will depend on the lattice parameters for the Mg-Al anionic clay. There are more differences in the X-ray diffraction pattern, but these are the best distinguishable reflections, because other compounds which are likely to be present in the Mg-Al anionic clay-like material hardly have reflections around 45-47° 2-theta. Although, boehmite has a weak reflection in that range, its presence can be excluded if its strong reflection between 13 and 15 degrees 2-theta is absent.
$3R_2$ type anionic clays appear to have a different morphology than $3R_1$ type anionic clays. The $3R_2$ type anionic clay appears to have a structure with irregular flake-lik platelets which are randomly agglomerated. Conventional

$3R_1$ type anionic clay has regular w ll-formed layers of platelets which are arranged in the usual bookstack form.

As mentioned before, also metal doped divalent and trivalent metal sources can be used for the preparation of metal doped anionic clays. Examples of such metal sources are metal doped (pseudo)boehmite, metal doped $Mg(OH)_2$, and metal doped MgO.

The anionic clay is doped with one or more metal dopants. Preferred metal dopants are compounds of the elements selected from the group of zinc, vanadium, iron, copper, tungsten, molybdenum, cobalt, niobium, nickel, chromium, cobalt, rare earth metals, e.g. lanthanum and/or cerium, and combinations thereof. More preferred elements are zinc, vanadium, iron, tungsten, molybdenum, cerium, and combinations thereof.

If more than one metal dopant is used, it is preferred to use a combination of a Zn-containing compound and a V-containing compound, a combination of a Zn-containing compound and a W-containing compound, a combination of a Ce-containing compound and a V-containing compound, a combination of a Fe-containing compound and a V-containing compound, a combination of Zn-containing compound, a V-containing compound and a W-containing compound, a combintalon of a Fe-containing compound and a Ce-containing compound, or a combination of a Mo-containing compound and a W-containing compound.

Suitable compounds containing the desired elements are their nitrates, sulphates, chlorides, formates, acetates, oxalates, alkoxides, carbonates, vanadates, molybdates, borates, phosphates, etc.

The metal dopant(s) is/are preferably present in the anionic clay in amounts of less than 70 wt%, more preferably between 2 and 50 wt%, even more preferably between 2 and 30 wt% and most preferably between 2 and 20 wt%, calculated as metal oxide and based on the weight of metal doped anionic clay.

If desired, the metal doped anionic clay may be subjected to ion-exchange. Upon ion-exchange the interlayer charge-balancing anions are replaced with other anions. Said other anions are the ones commonly present in anionic clays and include pillaring anions such as $V_2O_7^{4-}$, $HV_2O_{12}^{4-}$, $V_3O_9^{3-}$, $V_{10}O_{28}^{-6}$, $Mo_7O_{24}^{6-}$, $PW_{12}O_{40}^{3-}$, $B(OH)_4^{-}$, $[B_3O_3(OH)_4]^{-}$, $[B_3O_3(OH)_5]^{2-}$, $B_4O_5(OH)_4^{2-}$, HBO_4^{2-}, $HGaO_3^{2-}$, CrO_4^{2-}, Keggin-ions, formate, acetate, phosphates, tungstates, and mixtures thereof. Examples of suitable pillaring anions are given in US 4,774,212 which is included by reference for this purpose. Said ion-exchange can be conducted before or after drying the anionic clay-containing composition formed in the suspension.

Zeolites

Preferred zeolites to be used in the catalyst composition of the present invention are pentasil zeolites (e.g.ZSM-5, zeolite beta) optionally containing phosphate, rare earth metal(s) (e.g. RE-ZSM-5), and/or transition metal(s) such as Fe , V, and Zn, and/or faujasite zeolites (e.g. zeolite X, Y, LZ-210), optionally ultrastabilized (USY), dealuminated, and/or exchanged with alkaline earth metals, transition metals, and/or rare-earth metals. The preferred zeolite is a rare earth exchanged zeolite Y or USY with a SAR between 4.0 and 6.0, preferably between 5.0 and 6.0.

Aluminas

Suitable aluminas or alumina sources for the present invention include boehmite, e.g. quasi-crystalline or microcrystalline boehmite, alumina gel, alumina sol, aluminium chlorohydrol, or aluminium nitrohydrol. The alumina may be peptised with (in)organic acids.

Both the metal doped anionic clay and the alumina can serve as matrix material.

Silica

The composition optionally contains silica. Suitable silica sources are silica gels, silica sols, and Si-Al co-gels. A preferred silica source is silica hydrosol. Silica hydrosols can be prepared by neutralisation of an acidic sodium silicate solution or by ion-exchange of sodium silicate.

The presence of silica is especially preferred if pseudoboehmite is used as matrix material.

Kaolin

The term 'kaolin' includes any form of kaolin, such as metakaolin, calcined kaolin, leached kaolin, dealuminated kaolin, etc.

Other ingredients

The composition may also contain other ingredients frequently used in FCC catalysts, such as metal traps, CO combustion promotors, etc. Examples of such other ingredients include alumina-titania, titania, zirconia, cationic clay, alkaline earth metal (hydr)oxides, boron, phosphates, aluminium phosphates, palladium, and platinum.

The term 'cationic clay' includes smectites (e.g. saponite, montmorillonite, bentonite, laponite, hectorite), phosphated smectites, calcined smectites, leached smectites and/or dealuminated smectites.

The catalyst composition according to the present invention comprises 5-55 wt% metal doped anionic clay, 10-50 wt% zeolite, 5-40 wt% alumina, 0-10 wt% silica, 0-10 wt% of other ingredients, and balance kaolin.

Preferably, the composition comprises 10-35 wt% of metal doped anionic clay, 20-30 wt% of zeolite, 10-30 wt% alumina, 0-10 wt% of silica, 0-10 wt% of other ingredients, and balance kaolin.

Preparation of the catalyst composition

The catalyst composition according to the invention can be prepared by mixing zeolite, metal doped anionic clay, alumina, kaolin, and the optional silica in an aqueous suspension, followed by shaping the material to form particles. Shaping is preferably performed by spray-drying.

The ingredients can be added to the suspension as powder, as a shaped body, or as an aqueous suspension. The ingredients can be milled before addition to the suspension. Alternatively, they can be milled together while present in the suspension.

Other ingredients, such as metal traps or combustion promoters, pore regulating agents, cationic clays, and other known additives used in FCC catalyst preparation including phosphates may be added to the aqueous suspension mentioned above, or they may be impregnated on the shaped catalyst.

The pH of the suspension is preferably between 4 and 8, more preferably between 5 and 7.

The final catalyst particles preferably have an average particle size of 50-100 microns, which makes them suitable for use in FCC units.

The catalyst composition is very suitable for the production of fuels, such as gasoline and diesel, with relatively low sulfur and nitrogen content. The catalyst composition is especially suitable for the production of said fuels from resid-containing oil feeds.

Figure 1 shows an X-ray diffraction pattern of a non-doped, non-impregnated anionic clay.

Figure 2 shows an X-ray diffraction pattern of a Zn-impregnated anionic clay.

Figure 3 shows an X-ray diffraction pattern of a Zn-doped anionic clay, whereby the Zn was introduced during rehydration.

Figure 4 shows an X-ray diffraction pattern of a Zn-doped anionic clay, whereby the Zn was present during aging.

Figure 5 shows an electron microscopy photograph of a Ce-impregnated anionic clay.

Figure 6 shows an electron microscopy photograph of a Ce-doped anionic clay.

EXAMPLES

Comparative Example 1

An anionic clay was prepared by suspending 1250 g MgO and 1210 g flash-calcined gibbsite (Alcoa CP-3®) in 7540 g water. This mixture was aged at 170 °C for 1 hour under autogeneous pressure. The suspension was filtered and th product was dried at 120°C.

The X-ray diffraction pattern of the resulting non-doped, non-impregnated Mg-Al anionic clay is presented in Figure 1.

A catalyst was prepared by slurrying 10 wt% (on dry base) of the anionic clay with 25 wt% zeolite, 30 wt% alumina, 5 wt% silicasol, and balance kaolin.

Comparative Example 2

An anionic clay was prepared according to Comparative Example 1. Th resulting anionic clay was impregnated with an aqueous solution of zinc nitrate, using pore volume impregnation. The resulting product had a Zn-content, calculated as ZnO, of 3.5 wt%, and is representative of the prior art WO 99/49001.

The X-ray diffraction pattern of the resulting Zn-impregnated Mg-Al anionic clay is presented in Figure 2. This pattern shows, compared to the pattern of non-doped and non-impregnated anionic clay (Figure 1), additional reflections at about 31.8, 34.4, 36.3, and 56.6 degrees 2-theta (indicated by: *). These additional reflections indicate the presence of a separate ZnO-phase.

A catalyst was prepared by slurrying 10 wt% (on dry bas) of the Zn-impregnated anionic clay with 25 wt% zeolite, 30 wt% alumina, 5 wt% silica sol, and balance kaolin.

Example 3

An anionic clay was prepared according to Comparative Example 1. The anionic clay was calcined and subsequently rehydrated in the presence of zinc nitrate. The resulting doped anionic clay had a Zn-content, calculated as ZnO, of 3.5 wt%.

The X-ray diffraction pattern of the resulting Zn-doped Mg-Al anionic clay is presented in Figure 3. It is clear that the separate ZnO-phase which was present in the Zn-impregnated anionic clay of Comparative Example 2 (Figure 2) is not present in this Zn-doped anionic clay. The diffraction pattern of the Zn-doped anionic clay is equivalent to the diffraction pattern of the non-doped non-impregnated anionic clay of Figure 1, indicating a more homogeneous distribution of the Zn-phase within the doped anionic clay compared to the impregnated anionic clay of Comparative Example 2.

A catalyst according to the invention was prepared by slurrying 10 wt% (on dry base) of the Zn-doped anionic clay with 25 wt% zeolite, 30 wt% alumina, 5 wt% silicasol, and balance kaolin.

Example 4

An anionic clay was prepared by suspending 1190 g MgO, 800 g FC-BOC (Alcoa CP-3®), and 300 g $Zn(NO_3)_2.6H_2O$ in 7500 g water. This mixture was aged at 170°C under autogeneous pressure for 1 hour. The suspension was filtered and the product was dried at 120°C. The resulting doped anionic clay had a Zn-content, calculated as ZnO, of 4 wt%.

The X-ray diffraction pattern of the resulting Zn-doped Mg-Al anionic clay is presented in Figure 4. This pattern indicates the presence of anionic clay, boehmit , and brucite ($Mg(OH)_2$). A separate ZnO-phase was not detected, as

indicated by the absence of reflection at 31.8, 34.4, 36.3, and 56.6 degre s 2-theta. Hence, also this way of doping leads to a more homogeneous distribution of the Zn-phase within the product than impregnation.

A catalyst according to the invention was prepared by slurrying 10 wt% (on dry base) of the Zn-doped anionic clay with 25 wt% zeolite, 30 wt% alumina, 5 wt% silicasol, and balance kaolin.

Comparative Example 5

An anionic clay was prepared according to Comparative Example 1. The resulting anionic clay was impregnated with an aqueous solution of cerium nitrate, using pore volume impregnation. The resulting product had a Ce-content, calculated as CeO, of 11 wt%.
Figure 5 presents an electron microscopy photograph of this Ce-impregnated Mg-Al anionic clay, with the Ce-distribution indicated in white. It is clear the C is not homogeneously distributed in the anionic clay particles, but is mainly present on the outside of the particles.

Example 6

A Ce-doped anionic clay was prepared according to the method of Example 4, except that zinc nitrate was replaced by cerium nitrate. Figure 6 presents an electron microscopy photograph of this Ce-doped Mg-Al anionic clay, with the Ce-distribution indicated in white. It is clear the Ce in this clay is more homogeneously distributed that in the Ce-impregnated anionic clay of Comparative Example 5.

Example 7

The catalyst composition according to Example 4 and Comparative Examples 1 and 2 were tested in an FCC unit. The sulphur concentration in the resulting gasoline at 65 wt% conversion amounted to 1434, 1759, and 1735 ppmw, respectively. Hence, the use of a Zn-doped anionic clay resulted in a sulphur

reduction which was 17% higher than the sulphur reduction resulting from th use of a Zn-impregnated anionic clay.

CLAIMS

1. Catalyst composition comprising 5-55 wt% metal doped anionic clay, 10-50 wt% zeolite, 5-40 wt% alumina, 0-10 wt% silica, 0-10 wt% of other ingredients, and balance kaolin.

2. Catalyst composition according to claim 1 wherein the anionic clay is doped with at least one compound containing an element selected from the group of Zn, Fe, V, Cu, W, Mo, Co, Nb, Ni, Cr, Ce, and La.

3. Catalyst composition according to any one of the preceding claims wherein the anionic clay is an Al-Mg-containing anionic clay, a Al-containing non-Mg anionic clay, a Mg-containing non-Al anionic clay, or a non-Mg non-Al anionic clay.

4. Process for the preparation of a catalyst composition according to any one of the preceding claims wherein zeolite, metal doped anionic clay, alumina, kaolin, and optionally silica and other ingredients are mixed in aqueous suspension and subsequently shaped to form particles.

5. Process according to claim 4 wherein the metal doped anionic clay is prepared by co-precipitating a trivalent metal source, a divalent metal source and at least one metal dopant out of an aqueous solution.

6. Process according to claim 4 wherein the metal doped anionic clay is prepared by mixing a trivalent metal source and a divalent metal source in aqueous suspension and aging the mixture in the presence of at least on metal dopant.

7. Process according to claim 4 wherein the metal doped anionic clay is prepared by aging a trivalent metal source and a divalent metal source in

aqueous suspension to form an anionic clay, thermally treating the anionic clay to form a solid solution, and rehydrating the solid solution in th presence of at least one metal dopant to form a metal doped anionic clay.

8. Process according to claim 4 wherein the metal doped anionic clay is prepared by mixing a trivalent metal source, a divalent metal source and at least one metal dopant in aqueous suspension, shaping the mixture to form a shaped body, and aging the shaped body in the presence of at least one metal dopant.

9. Process according to any one of claims 5-8 wherein the trivalent metal is selected from the group consisting of aluminium, gallium, indium, iron, chromium, vanadium, cobalt, manganese, cerium, niobium, lanthanum, and combinations thereof.

10. Process according to any one of claims 5-9 wherein the divalent metal is selected from the group consisting of magnesium, zinc, nickel, copper, iron, cobalt, manganese, calcium, barium, and combinations thereof.

11. Process according to claim 9 or 10 wherein the divalent metal source and/or the trivalent metal source is/are selected from the group consisting of oxides, hydroxides, carbonates, hydroxycarbonates, bicarbonates, acetates, and hydroxyacetates.

12. Process according to any one of the claims 5-11, wherein a metal doped divalent and/or metal doped trivalent metal source is used.

13. Use of a catalyst composition according to any one of the claims 1-3 for the production of gasoline and/or diesel having a reduced sulphur content and/or a reduced nitrogen content.

ABSTRACT

The present invention relates to a catalyst composition comprising 5-55 wt% metal doped anionic clay, 10-50 wt% zeolite, 5-40 wt% alumina, 0-10 wt% silica, 0-10 wt% of other ingredients, and balance kaolin.

In metal doped anionic clays, the additive, i.e. the metal dopant, is better distributed within the anionic clay than in impregnated anionic clays, without separate phases of additive being present. Hence, abrasion of this catalyst composition will result in microfines poorer in additive than the prior art composition.

Furthermore, the catalyst composition according to the invention results in a higher reduction of sulphur in fuels such as gasoline and diesel than compositions comprising impregnated anionic clay.

Figure 1/6

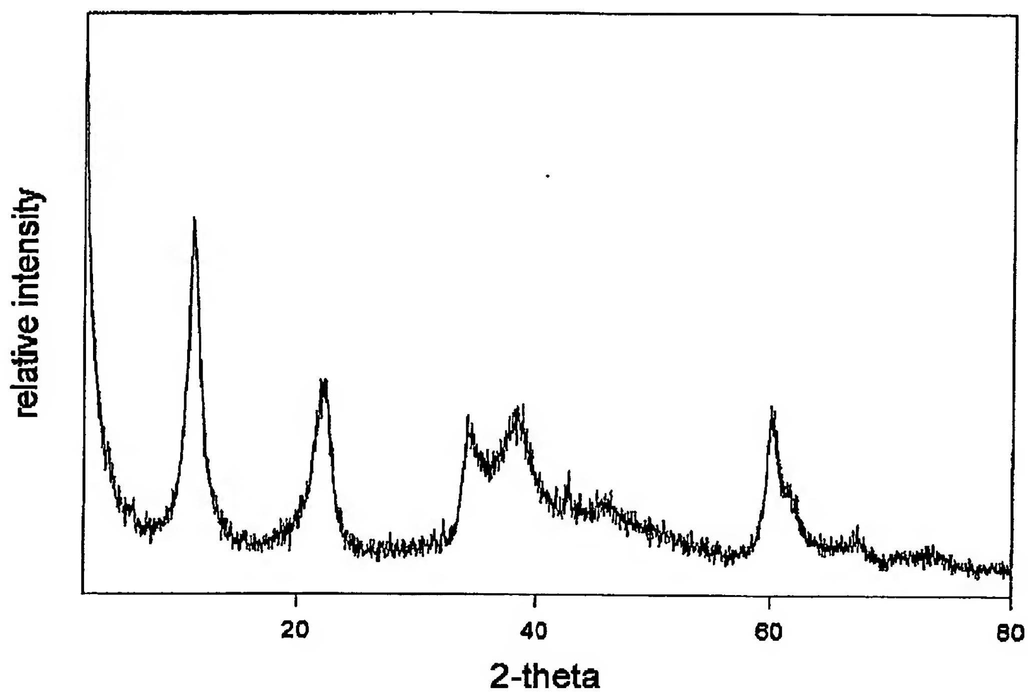

Figure 2/6

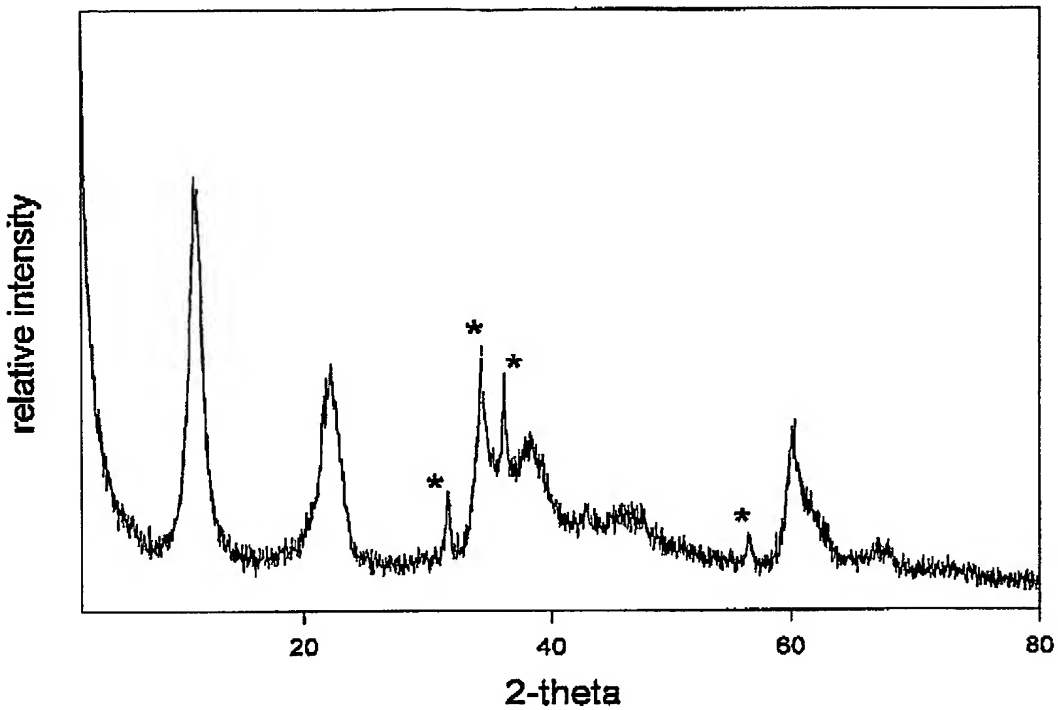

Figure 3/6

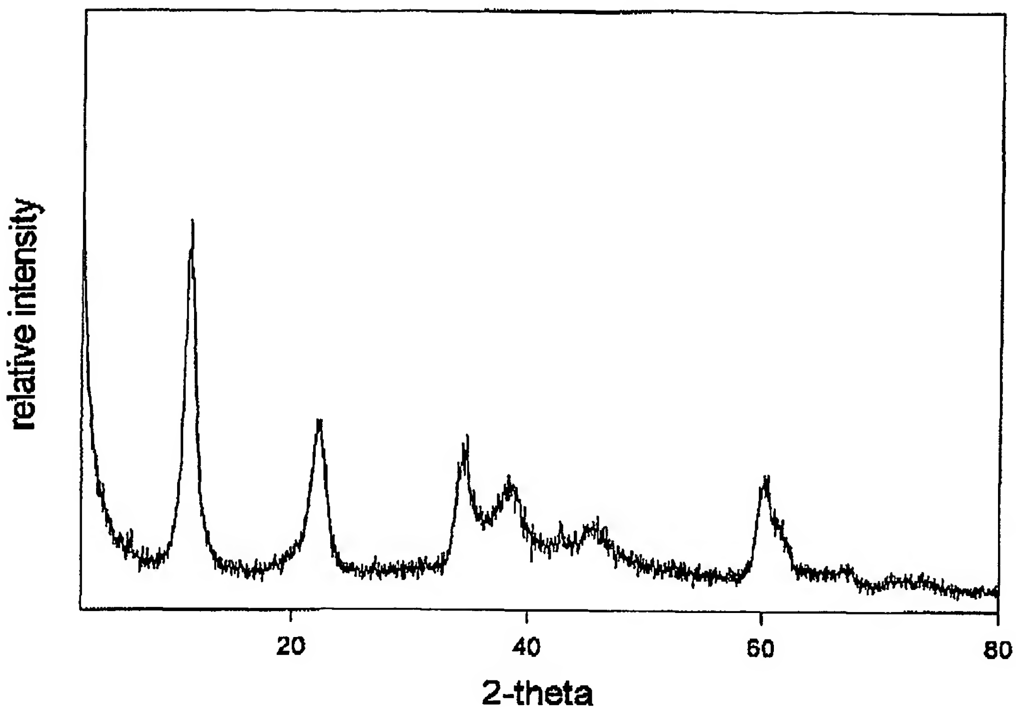

Figure 4/6

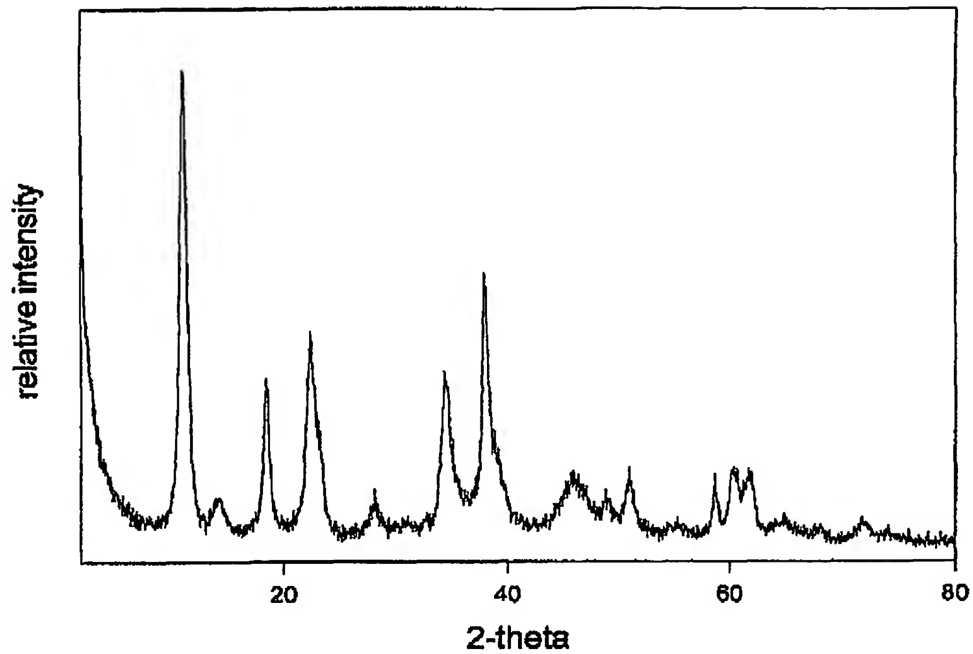

Figure 5/6

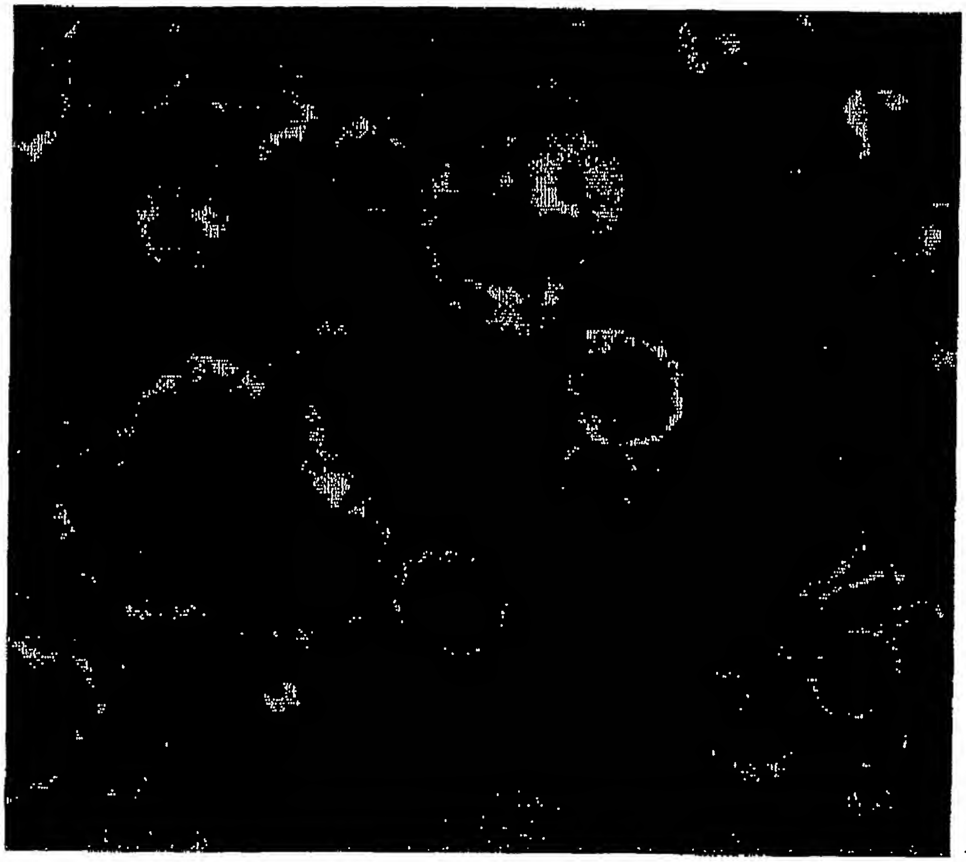

Figure 6/6